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(54) Title: SILICONE RUBBER COMPOSITIONS AND ELASTOMERIC MATERIALS

(57) Abstract: A composition and method for making a subsea insulation silicone rubber material are provided. The composition includes a particular organohydrogenpolysiloxane crosslinker.

SILICONE RUBBER COMPOSITIONS AND ELASTOMERIC MATERIALS

[0001] The present invention relates to a subsea insulation silicone elastomeric material for use on subsea oil and gas production equipment, a composition used in the making of the elastomeric material and articles made from the elastomeric material.

[0002] Subsea wells and pipelines are used globally in connection with the production of hydrocarbons, in the form of oil and/or gas. A well extends from the seabed to the required depth at which the hydrocarbon reservoir is located and recovery of the hydrocarbons from the well to the surface is typically carried out using pipes, often referred to as "subsea risers". Subsea risers extend from a well head or manifold on the seabed to a platform or vessel tethered on the surface above the well. It is not unusual for the risers to extend over hundreds or indeed thousands of meters between the wellhead and the surface.

[0003] In order for extraction to be viable a number of issues need to be dealt with not least insulation of the subsea risers, because of the temperature of the surrounding seawater to prevent restricted flow or even blockages of the hydrocarbons within the subsea risers between the well head and the platform/vessel and also the corrosive environment, i.e. the sea water itself.

[0004] In many subsea locations e.g. where subsea oil and gas wells are located at depths of 1500m or greater, the pipelines and wellhead equipment are exposed to seawater which is just a few degrees above freezing (e.g. about 4 to 5°C). In the absence of insulation hot produced hydrocarbon fluids within the production equipment are cooled by the surrounding seawater which, if the temperature of the fluids approach the seawater temperature, can result in hydrates and paraffin waxes being formed within the pipe line consequentially causing a restriction of hydrocarbon flow or even blockages within the pipelines. Hence, the application of thermal insulation to subsea oil and gas equipment to minimise the reduction in temperature of the hydrocarbons whilst being transported through the pipeline is essential both for the technical feasibility and practical viability of deep sea extraction with the benefits including, for example:-

(i) a higher production rate by maintaining high oil temperature and increasing flow rates;

(ii) lower processing costs by elimination of the requirement to reheat crude oil for water separation upon its arrival at the platform;

(iii) prevention of hydrate and wax formation by maintaining the oil temperature above that at which hydrates form, in turn eliminating pipe blockages which would increase production costs;

(iv) elimination of the need for methanol injection to overcome the problems described above; and

(v) reduction in the requirement for internal cleaning of pipes.

[0005] Suitable insulation materials also need to be unaffected by the extreme temperatures of the hydrocarbon fluids exiting the well. In some cases the temperature of the exiting fluids may reach

150°C or higher, and the fluids will consequently heat both the surrounding equipment and the insulation. Therefore, any insulation material which is used on such wells must be able to withstand these extreme temperatures without detriment to its thermal or mechanical properties.

[0006] Furthermore, given the seawater surrounding a riser forms a corrosive environment through which the riser must extend and over time any damage to the outer surface of the riser can allow seawater to permeate into the layers of the riser and from there into the hydrocarbon stream, or alternatively, can allow the hydrocarbons flowing in the riser to leak into the surrounding seawater. The corrosive effects of the seawater are particularly evident in the area immediately below the surface of the sea, up to a depth of about 50m because it can be subjected to the effects of weather and turbulence under the surface due to prevailing weather conditions.

[0007] To perform successfully in this environment, a thermal insulation material must have a low thermal conductivity, exhibit acceptable mechanical properties such as flexibility and impact resistance, and be economical to install and preferably should be resistant to the corrosive nature of the seawater.

[0008] A variety of insulation materials for this application are known, for example syntactic phenolic foams and high temperature epoxy resins have been used because they can withstand these relatively high temperatures but unfortunately they are inherently brittle and as such are unable to meet the flexibility and impact resistance requirements. Furthermore, because of their brittle nature and exothermic curing properties, these materials are difficult and expensive to install and repair.

[0009] Other prior art insulating materials used include amine cured epoxies, urethanes and polypropylenes, however whilst these exhibit acceptable flexibility and impact resistance characteristics they are unable to withstand the relatively high flow temperatures of the hydrocarbons being extracted.

[0010] Liquid silicone rubber based materials made using organopolysiloxane polymers having viscosities of up to about 500,000 mPa.s at 25°C have been utilised for subsea insulation but whilst having advantages over the above because of the ability to withstand wide temperature variations without an appreciable effect on their physical properties and being virtually unaffected by ultraviolet radiation, even over long periods of time, ozone, oil, salt, water and the like. They have had adhesion problems after exposure to the high temperatures of the hydrocarbons transported through the riser pipes.

[0011] Manufacturers therefore are continually seeking alternative improved solutions in improving the thermal stability of said hydrosilylation cured compositions so as to provide improved subsea insulation. A current cross-linker utilised is a short chain polymer mixture of the average formula $MD_{3.34}D'_{5.32}M$ where (M is Me_3Si-, D is $–OSiMe_2$-, D' is –OSiMe'H-), where the molar ratio of D : D'is 0.6 : 1; i.e.

Me_3Si-$[OSiMe_2]_{3.34}$-$[OSiMeH]_{5.32}$-Si Me_3.

It has been identified that such a cross-linker needs to be reacted with polydiorganosiloxane polymer(s) having at least 2 vinyl groups per molecule in a Si-H to Vinyl ratio of at least 2: 1, however, it has now been identified that the thermal stability of the resulting elastomers may be improved by the use of alternative cross-linkers.

[0012] There is provided a subsea insulation silicone rubber composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$$R^2_z\,(H)_{3-z}\text{-}Si\text{-}D^1_nD^2_mSi\,(H)_{3-z}\,R^2_z$$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is $-[OSiR_2]$ - and D^2 is $-[OSiRH]$-;

(iv) a hydrosilylation catalyst and optionally

(v) an organosilicate resin comprising $R^4_dR^2_{3-d}SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2; characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 :D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1.

[0013] The composition may include one or more optional additives but the total weight % of the composition is 100 wt. % and the unsaturated groups e.g. alkenyl and/or alkynyl content of polymer (i) is determined using quantitative infra-red analysis in accordance with ASTM E168. The degree of polymerisation (henceforth referred to as DP) is n + m +2

[0014] There is also provided an elastomeric subsea insulation silicone rubber material which is the cured product of a composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is –[$OSiR_2$] - and D^2 is –[OSiRH]-;

(iv) a hydrosilylation catalyst; and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{(3-d)} SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2;

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 :D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1.

[0015] There is further provided the use of a silicone rubber composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is $–[OSiR_2]$ - and D^2 is –[OSiRH]-;

(iv) a hydrosilylation catalyst; and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{(3-d)}SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2;

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 : D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1: D^2 is from 0.5 : 1 to 1 : 1;

to make an elastomeric subsea insulation silicone rubber material.

[0016] There is also provided an elastomeric subsea insulation silicone rubber material which is obtainable or obtained by curing a composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is $–[OSiR_2]$ - and D^2 is –[OSiRH]-;

(iv) a hydrosilylation catalyst; and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{(3-d)}SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein

R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2;

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 : D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1: D^2 is from 0.5 : 1 to 1 : 1.

[0017] There is also provided a method of preparing an elastomeric subsea insulation silicone rubber material which is the cured product of a composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers;

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is –[$OSiR_2$] - and D^2 is –[OSiRH]-; and

(iv) a hydrosilylation catalyst; and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{(3-d)} SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2;

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 : D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1: D^2 is from 0.5 : 1 to 1 : 1.

[0018] Component (i) is one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule. Polydiorganosiloxane polymer (i) has multiple units of the formula (I):

$$R_aSiO_{(4-a)/2} \quad (I)$$

in which each R is independently selected from an aliphatic hydrocarbyl, aromatic hydrocarbyl, or organyl group (that is any organic substituent group, regardless of functional type, having one free valence at a carbon atom). Saturated aliphatic hydrocarbyls are exemplified by, but not limited to alkyl groups such as methyl, ethyl, propyl, pentyl, octyl, undecyl, and octadecyl and cycloalkyl groups such as cyclohexyl. Unsaturated aliphatic hydrocarbyls are exemplified by, but not limited to, alkenyl groups such as vinyl, allyl, butenyl, pentenyl, cyclohexenyl and hexenyl; and by alkynyl groups. Aromatic hydrocarbon groups are exemplified by, but not limited to, phenyl, tolyl, xylyl, benzyl, styryl, and 2-phenylethyl. Organyl groups are exemplified by, but not limited to, halogenated alkyl groups such as chloromethyl and 3-chloropropyl; nitrogen containing groups such as amino groups, amido groups, imino groups, imido groups; oxygen containing groups such as polyoxyalkylene groups, carbonyl groups, alkoxy groups and hydroxyl groups. Further organyl groups may include sulfur containing groups, phosphorus containing groups and/or boron containing groups. The subscript "a" may be 0, 1, 2 or 3, but is typically mainly 2 or 3.

[0019] Siloxy units may be described by a shorthand (abbreviated) nomenclature, namely - "M," "D," "T," and "Q", when R is an organic group, typically methyl group (further teaching on silicone nomenclature may be found in Walter Noll, Chemistry and Technology of Silicones, dated 1962, Chapter I, pages 1-9). The M unit corresponds to a siloxy unit where a = 3, that is $R_3SiO_{1/2}$; the D unit corresponds to a siloxy unit where a = 2, namely $R_2SiO_{2/2}$; the T unit corresponds to a siloxy unit where a = 1, namely $R_1SiO_{3/2}$; the Q unit corresponds to a siloxy unit where a = 0, namely $SiO_{4/2}$.

[0020] Examples of typical groups on the polydiorganosiloxane polymer (i) include mainly alkenyl, alkyl, and/or aryl groups. The groups may be in pendent position (on a D or T siloxy unit), or may be terminal (on an M siloxy unit). As previously indicated alkenyl and/or alkynyl groups are essential when the composition is being cured by hydrosilylation but are optional if the sole curing agent for the cure process is a peroxide. Hence, suitable alkenyl groups in polydiorganosiloxane polymer (i) typically contain from 2 to 10 carbon atoms, e.g. vinyl, isopropenyl, allyl, and 5-hexenyl.

[0021] The silicon-bonded organic groups attached to polydiorganosiloxane polymer (i) other than alkenyl groups and/or alkynyl groups are typically selected from monovalent saturated hydrocarbon groups, which typically contain from 1 to 10 carbon atoms, and monovalent aromatic hydrocarbon groups, which typically contain from 6 to 12 carbon atoms, which are unsubstituted or substituted with groups that do not interfere with curing of this inventive composition, such as halogen atoms. Preferred

species of the silicon-bonded organic groups are, for example, alkyl groups such as methyl, ethyl, and propyl; and aryl groups such as phenyl.

[0022] The molecular structure of polydiorganosiloxane polymer (i) is typically linear, however, there can be some branching due to the presence of T units (as previously described) within the molecule.

[0023] To achieve a useful level of physical properties in the elastomer prepared by curing the composition as hereinbefore described the viscosity of polydiorganosiloxane polymer (i) should be at least 1000mPa.s at 25 °C. The upper limit for the viscosity of polydiorganosiloxane polymer (i) is limited to a viscosity of up to 500,000mPa.s at 25°C.

[0024] Generally, the or each polydiorganosiloxane containing at least two silicon-bonded alkenyl groups per molecule of ingredient (a) has a viscosity of from 1000 mPa.s to 150,000mPa.s at 25 °C, alternatively from 2000mPa.s to 125,000mPa.s, alternatively from 2000mPa.s to 100,000mPa.s at 25 °C measured in accordance with ASTM D 1084-16 using a Brookfield rotational viscometer with the most appropriate spindle for the viscosity being measured at 1 rpm, unless otherwise indicated.

[0025] The polydiorganosiloxane polymer (i) may be selected from polydimethylsiloxanes, alkylmethylpolysiloxanes, alkylarylpolysiloxanes or copolymers thereof containing e.g. alkenyl and/or alkynyl groups and may have any suitable terminal groups, for example, they may be trialkyl terminated, alkenyldialkyl terminated or may be terminated with any other suitable terminal group combination providing each polymer contains at least two alkenyl groups and/or alkynyl groups per molecule. Hence the Polydiorganosiloxane polymer (i) may be, for the sake of example, dimethylvinyl terminated polydimethylsiloxane, dimethylvinylsiloxy-terminated dimethylmethylphenylsiloxane, trialkyl terminated dimethylmethylvinyl polysiloxane or dialkylvinyl terminated dimethylmethylvinyl polysiloxane copolymers.

[0026] For example, a polydiorganosiloxane polymer (i) containing alkenyl groups and/or alkynyl groups at the two terminals may be represented by the general formula (II):

$R'R"R"'SiO-(R"R"'SiO)_m-SiOR"'R"R'$ (II)

[0027] In formula (II), each R' may be an alkenyl group or an alkynyl group, which typically contains from 2 to 10 carbon atoms. Alkenyl groups include but are not limited to vinyl, propenyl, butenyl, pentenyl, hexenyl an alkenylated cyclohexyl group, heptenyl, octenyl, nonenyl, decenyl or similar linear and branched alkenyl groups and alkenylated aromatic ringed structures. Alkynyl groups may be selected from but are not limited to ethynyl, propynyl, butynyl, pentynyl, hexynyl an alkynylated cyclohexyl group, heptynyl, octynyl, nonynyl, decynyl or similar linear and branched alkenyl groups and alkenylated aromatic ringed structures.

[0028] R" does not contain ethylenic unsaturation, Each R" may be the same or different and is individually selected from monovalent saturated hydrocarbon group, which typically contain from 1

to 10 carbon atoms, and monovalent aromatic hydrocarbon group, which typically contain from 6 to 12 carbon atoms. R" may be unsubstituted or substituted with one or more groups that do not interfere with curing of this inventive composition, such as halogen atoms. R"' is R' or R".

[0029] Organopolysiloxane polymer (i), is typically present in an amount of from 40 to 80 wt% of the composition. When resin (v) is present in the composition organopolysiloxane polymer (i) is generally present in an amount of from 40 to 60% by weight of the composition, but in the absence of resin (v), organopolysiloxane polymer (i) may be present in an amount of from 50 to 75% by weight of the composition.

(ii) Reinforcing filler

[0030] Component (ii) of the composition is a reinforcing filler such as finely divided silica. Silica and other reinforcing fillers (ii) are often treated with one or more known filler treating agents to prevent a phenomenon referred to as "creping" or "crepe hardening" during processing of the curable composition.

[0031] Finely divided forms of silica are preferred reinforcing fillers (ii). Colloidal silicas are particularly preferred because of their relatively high surface area, which is typically at least 50 m^2/g (BET method in accordance with ISO 9277: 2010). Fillers having surface areas of from 50 to 450 m^2/g (BET method in accordance with ISO 9277: 2010), alternatively of from 50 to 300 m^2/g (BET method in accordance with ISO 9277: 2010), are typically used. For the avoidance of doubt colloidal silicas as described herein may be can be provided in the form of precipitated silica and/or fumed silica. Both types of silica are commercially available.

[0032] The amount of reinforcing filler (ii) e.g. finely divided silica in the composition herein is from 5 to 40%wt, alternatively of from 5 to 30%wt. In some instances, the amount of reinforcing filler may be of from 7.5 to 30% wt., alternatively from 10 to 30% wt. based on the weight of the composition, alternatively from 15 to 30% wt. based on the weight of the composition.

[0033] When reinforcing filler (ii) is naturally hydrophilic (e.g. untreated silica fillers), it is typically treated with a treating agent to render it hydrophobic. These surface modified reinforcing fillers (ii) do not clump, and can be homogeneously incorporated into polydiorganosiloxane polymer (i) as the surface treatment makes the fillers easily wetted by polydiorganosiloxane polymer (i). This results in improved room temperature mechanical properties of the compositions and resulting cured materials cured therefrom.

[0034] The surface treatment may be undertaken prior to introduction in the composition or in situ (i.e. in the presence of at least a portion of the other ingredients of the composition herein by blending these ingredients together at room temperature or above until the filler is completely treated. Typically, untreated reinforcing filler (ii) is treated in situ with a treating agent in the presence of polydiorganosiloxane polymer (i), whereafter mixing, a silicone rubber base material is obtained, to which other ingredients may be added.

[0035] Typically reinforcing filler (ii) may be surface treated with any low molecular weight organosilicon compounds disclosed in the art applicable to prevent creping of organosiloxane compositions during processing. For example organosilanes, polydiorganosiloxanes, or organosilazanes e.g. hexaalkyl disilazane, short chain siloxane diols or fatty acids or fatty acid esters such as stearates to render the filler(s) hydrophobic and therefore easier to handle and obtain a homogeneous mixture with the other ingredients. Specific examples include but are not restricted to silanol terminated trifluoropropylmethyl siloxane, silanol terminated ViMe siloxane, tetramethyldi(trifluoropropyl)disilazane, tetramethyldivinyl disilazane, silanol terminated MePh siloxane, liquid hydroxyl-terminated polydiorganosiloxane containing an average from 2 to 20 repeating units of diorganosiloxane in each molecule, hexaorganodisiloxane, hexaorganodisilazane. A small amount of water can be added together with the silica treating agent(s) as processing aid.

[0036] The composition may include one or more optional additives but the total weight % of the composition is 100 wt. % and the alkenyl and/or alkynyl content of polymer (i) is determined using quantitative infra-red analysis in accordance with ASTM E168.

[0037] The composition as described herein is cured using a hydrosilylation cure package comprising an organohydrogenpolysiloxane having 3 or more silicon-bonded hydrogen atoms per molecule and a hydrosilylation catalyst.

iii) Organohydrogenpolysiloxane Cross-linker

[0038] The organohydrogenpolysiloxane(s) having at least 2, alternatively at least 3 Si-H groups per molecule (iii), which operate(s) as cross-linker(s) for polydiorganosiloxane polymer (i) and resin (v), when the cross-linker is present, is of the following structure

$$R^2_z\,(H)_{3-z}\text{-}Si\text{-}D^1_nD^2_mSi\,(H)_{3-z}\,R^2_z$$

wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is –$[OSiR_2]$- and D^2 is –[OSiRH]-.

Said organohydrogenpolysiloxane(s) having at least 2, alternatively at least 3 Si-H groups per molecule (iii), will undergo a hydrosilylation (addition) reaction by way of its silicon-bonded hydrogen atoms with the alkenyl groups and/or alkynyl groups in polydiorganosiloxane polymer (i) catalysed by one or more hydrosilylation catalysts discussed below. The organohydrogenpolysiloxane (iii) normally contains 3 or more silicon-bonded hydrogen atoms per molecule so that the hydrogen atoms of this ingredient can sufficiently react with the alkenyl groups and/or alkynyl groups of polydiorganosiloxane polymer (i) to form a network structure therewith and thereby cure the composition.

[0039] The molecular configuration of the organohydrogenpolysiloxane (iii) requires either:

(a) the molar ratio of Si-H to unsaturated groups (e.g.alkenyl and alkynyl, typically Vinyl) is < 1.5 : 1, alternatively , 1.35 : 1 and the molar ratio of D^1 : D^2 is > 1 : 1, alternatively > 1.25 : 1 or any suitable combination thereof; or

(b) the degree of polymerisation of cross-linker (iii) is > 20, alternatively > 30, alternatively > 40 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1, alternatively from 0.5 : 1 to 0.8 : 1 or any suitable combination thereof.

For the avoidance of doubt reference to unsaturated groups refers to the combination of alkenyl groups and alkynyl groups. Given the above the viscosity of the organohydrogen polysiloxane (iii) is typically from 0.001 to 50 Pa.s at 25 °C measured in accordance with ASTM D 1084-16 using a Brookfield rotational viscometer with the most appropriate spindle for the viscosity being measured at 1 rpm, unless otherwise indicated.

[0040] The cross-linkers (organohydrogenpolysiloxane(s) having at least 2, alternatively at least 3 Si-H groups per molecule) (iii) are present in the range described above, i.e. dependent on the molar ratio of silicon bonded hydrogen atoms to Vi groups discussed above but in terms of weight % they will typically be present in the composition in an amount somewhere within the approximate range of 2 to 10 weight% of the composition but this may vary depending on the cross-linker chosen and the ratios identified above.

iv) Hydrosilylation catalyst

[0041] As hereinbefore described the composition is cured via a hydrosilylation reaction catalysed by a hydrosilylation (addition cure) catalyst (iv) that is a metal selected from the platinum metals, i.e. platinum, ruthenium, osmium, rhodium, iridium and palladium, or a compound of such metals. The metals include platinum, palladium, and rhodium but platinum and rhodium compounds are preferred due to the high activity level of these catalysts for hydrosilylation reactions.

[0042] Example of preferred hydrosilylation catalysts (iv) include but are not limited to platinum black, platinum on various solid supports, chloroplatinic acids, alcohol solutions of chloroplatinic acid, and complexes of chloroplatinic acid with ethylenically unsaturated compounds such as olefins and organosiloxanes containing ethylenically unsaturated silicon-bonded hydrocarbon groups. The catalyst (iv) can be platinum metal, platinum metal deposited on a carrier, such as silica gel or powdered charcoal, or a compound or complex of a platinum group metal.

[0043] For example, suitable platinum based catalysts (iv) include

(i) complexes of chloroplatinic acid with organosiloxanes containing ethylenically unsaturated hydrocarbon groups are described in US 3,419,593;

(ii) chloroplatinic acid, either in hexahydrate form or anhydrous form;

(iii) a platinum-containing catalyst which is obtained by a method comprising reacting chloroplatinic acid with an aliphatically unsaturated organosilicon compound, such as divinyltetramethyldisiloxane;

(iv) alkene-platinum-silyl complexes as described in US Pat. No. 6,605,734 such as $(COD)Pt(SiMeCl_2)_2$ where "COD" is 1,5-cyclooctadiene; and/or

(v) Karstedt's catalyst, a platinum divinyl tetramethyl disiloxane complex typically containing about 1 wt.% of platinum in a solvent, such as toluene may be used. These are described in US3,715,334 and US3,814,730.

[0044] The hydrosilylation catalyst (iv) is present in the total composition in a catalytic amount, i.e., an amount or quantity sufficient to promote a reaction or curing thereof at desired conditions. Varying levels of the hydrosilylation catalyst (iv) can be used to tailor reaction rate and cure kinetics. The catalytic amount of the hydrosilylation catalyst (iv) is generally between 0.01 ppm, and 10,000 parts by weight of platinum-group metal, per million parts (ppm), based on the combined weight of the components (i) and (ii) and (v) when present; alternatively between 0.01 and 5000ppm; alternatively between 0.01 and 3,000 ppm, and alternatively between 0.01 and 1,000 ppm. In specific embodiments, the catalytic amount of the catalyst may range from 0.01 to 1,000 ppm, alternatively 0.01 to 750 ppm, alternatively 0.01 to 500 ppm and alternatively 0.01 to 100 ppm of metal based on the weight of the composition. The ranges may relate solely to the metal content within the catalyst or to the catalyst altogether (including its ligands) as specified, but typically these ranges relate solely to the metal content within the catalyst. The catalyst may be added as a single species or as a mixture of two or more different species. Typically, dependent on the form/concentration in which the catalyst package is provided the amount of catalyst present will be within the range of from 0.001 to 3.0% by weight of the composition.

Optional organosilicate resin (v)

[0045] The composition may also contain an organosilicate resin (v) comprising $R^4_dR^2_{3-d}SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2. The organosilicate resins (v) when present is a source of unsaturation in the form of alkenyl or alkynyl groups having from 2 to 10 carbons which are reactive with organohydrogenpolysiloxane (iii).

[0046] In the formula for organosilicate resin (v), R^2 is as described above. Examples of suitable alkyl groups include methyl, ethyl, propyl, pentyl, octyl and decyl groups. R^4 is an alkenyl and/or alkynyl group having from 2 to 10 carbons, alternatively having from 2 to 6 carbons for example vinyl, propenyl, hexenyl, ethynyl, propynyl and hexynyl groups, alternatively vinyl groups. Whilst d may be 0, 1 or 2, typically d is 1 or 2, alternatively d is 1.

[0047] The resinous portion of Organosilicate resin (v) has a weight average molecular weight (M_W) of 3,000 to 30,000g/mol when measured by gel permeation chromatography (GPC). Organosilicate resin (v) can be prepared by any suitable well-known method.

Additives

[0048] Additives may be present in the composition depending on the intended use of the curable silicone elastomer composition. For example, given the composition is cured via hydrosilylation, inhibitors designed to inhibit the reactivity of the hydrosilylation catalysts may be utilised. Other examples of optional additives include non-reinforcing fillers, electrical conductive fillers, thermally conductive fillers, non-conductive filler, pot life extenders, flame retardants, pigments, colouring agents, adhesion promoters, chain extenders heat stabilizers, compression set improvement additives and mixtures thereof.

Inhibitor

[0049] To obtain a longer working time or pot life of the silicone rubber composition when a dual cure system is being utilised, a suitable inhibitor may be incorporated into the composition in order to retard or suppress the activity of the catalyst.

[0050] Inhibitors of platinum metal based catalysts, generally a platinum metal based catalyst are well known in the art. Hydrosilylation or addition-reaction inhibitors include hydrazines, triazoles, phosphines, mercaptans, organic nitrogen compounds, acetylenic alcohols, silylated acetylenic alcohols, maleates, fumarates, ethylenically or aromatically unsaturated amides, ethylenically unsaturated isocyanates, olefinic siloxanes, unsaturated hydrocarbon monoesters and diesters, conjugated ene-ynes, hydroperoxides, nitriles, and diaziridines. Alkenyl-substituted siloxanes as described in US 3,989,667 may be used, of which cyclic methylvinylsiloxanes are preferred.

[0051] Another class of known inhibitors of platinum catalysts includes the acetylenic compounds disclosed in US 3,445,420. Acetylenic alcohols such as 2-methyl-3-butyn-2-ol constitute a preferred class of inhibitors that will suppress the activity of a platinum-containing catalyst at 25 °C. Compositions containing these inhibitors typically require heating at temperature of 70 °C or above to cure at a practical rate.

[0052] Examples of acetylenic alcohols and their derivatives include 1-ethynyl-1-cyclohexanol (ETCH), 2-methyl-3-butyn-2-ol, 3-butyn-1-ol, 3-butyn-2-ol, propargylalcohol, 2-phenyl-2-propyn-1-ol, 3,5-dimethyl-1-hexyn-3-ol, 1-ethynylcyclopentanol, 1-phenyl-2-propynol, 3-methyl-1-penten-4-yn-3-ol, and mixtures thereof.

[0053] When present, inhibitor concentrations as low as 1 mole of inhibitor per mole of the metal of catalyst (iv) will in some instances impart satisfactory storage stability and cure rate. In other instances inhibitor concentrations of up to 500 moles of inhibitor per mole of the metal of catalyst (iv) are required. The optimum concentration for a given inhibitor in a given composition is readily determined by routine experimentation. Dependent on the concentration and form in which the

inhibitor selected is provided/available commercially, when present in the composition, the inhibitor is typically present in an amount of from 0.0125 to 10% by weight of the composition. Mixtures of the above may also be used.

Other Additives

[0054] Commonly used other additives may be present in the composition as and when required depending on the intended use of the curable silicone elastomer composition. Examples of additives include non-reinforcing fillers, electrical conductive fillers, thermally conductive fillers, non-conductive filler, pot life extenders, flame retardants, pigments, colouring agents, adhesion promoters, chain extenders, heat stabilizers, compression set improvement additives and mixtures thereof.

Non-reinforcing filler

[0055] Non-reinforcing filler, when present, may comprise crushed quartz, diatomaceous earths, barium sulphate, iron oxide, titanium dioxide and carbon black, wollastonite and platelet type fillers such as, graphite, graphene, talc, mica, clay, sheet silicates, kaolin, montmorillonite and mixtures thereof. Other non-reinforcing fillers which might be used alone or in addition to the above include aluminite, calcium sulphate (anhydrite), gypsum, calcium sulphate, magnesium carbonate, aluminium trihydroxide, magnesium hydroxide (brucite), graphite, copper carbonate, e.g. malachite, nickel carbonate, e.g. zarachite, barium carbonate, e.g. witherite and/or strontium carbonate e.g. strontianite.

[0056] Non-reinforcing fillers when present may alternatively or additionally be selected from aluminium oxide, silicates from the group consisting of olivine group; garnet group; aluminosilicates; ring silicates; chain silicates; and sheet silicates. The olivine group comprises silicate minerals, such as but not limited to, forsterite and Mg_2SiO_4. The garnet group comprises ground silicate minerals, such as but not limited to, pyrope; $Mg_3Al_2Si_3O_{12}$; grossular; and $Ca_2Al_2Si_3O_{12}$. Aluninosilicates comprise ground silicate minerals, such as but not limited to, sillimanite; Al_2SiO_5 ; mullite; $3Al_2O_3.2SiO_2$; kyanite; and Al_2SiO_5.The ring silicates group comprises silicate minerals, such as but not limited to, cordierite and $Al_3(Mg,Fe)_2[Si_4AlO_{18}]$. The chain silicates group comprises ground silicate minerals, such as but not limited to, wollastonite and $Ca[SiO_3]$.

[0057] Suitable sheet silicates e.g. silicate minerals which may be utilised include but are not limited to mica; $K_2AI_{14}[Si_6Al_2O_{20}](OH)_4$; pyrophyllite; $Al_4[Si_8O_{20}](OH)_4$; talc; $Mg_6[Si_8O_{20}](OH)_4$; serpentine for example, asbestos; Kaolinite; $Al_4[Si_4O_{10}](OH)_8$; and vermiculite. When present, the non-reinforcing filler(s) is/are present up to a cumulative total of from 1 to 50% wt. of the composition.

[0058] In one embodiment the non-reinforcing filler may include glass or the like micro beads or microspheres to enhance the thermal insulation of the material. The micro beads or microspheres may be glass e.g. for example borosilicate glass micro-beads and/or microspheres.

[0059] Whenever deemed necessary the non-reinforcing filler may also be treated as described above with respect to the reinforcing fillers (ii) to render them hydrophobic and thereby easier to handle and obtain a homogeneous mixture with the other components. As in the case of the reinforcing fillers (ii) surface treatment of the non-reinforcing fillers makes them easily wetted by polydiorganosiloxane polymer (i) and resin (v) when present which may result in improved properties of the compositions, such as better processability (e.g. lower viscosity, better mold releasing ability and/or less adhesive to processing equipment, such as two roll mill), heat resistance, and mechanical properties.

[0060] Examples of electrical conductive fillers include metal particles, metal oxide particles, metal-coated metallic particles (such as silver plated nickel), metal coated non-metallic core particles (such as silver coated talc, or mica or quartz) and a combination thereof. Metal particles may be in the form of powder, flakes or filaments, and mixtures or derivatives thereof.

[0061] Examples of thermally conductive fillers include boron nitride, aluminium nitride, silicon carbide, metal oxides (such as zinc oxide, magnesium oxide, and aluminium oxide, graphite, diamond, and mixtures or derivatives thereof.

[0062] Examples of non-conductive fillers include quartz powder, diatomaceous earth, talc, clay, mica, calcium carbonate, magnesium carbonate, hollow glass, glass fibre, hollow resin and plated powder, and mixtures or derivatives thereof.

[0063] Pot life extenders, such as triazole, may be used, but are not considered necessary in the scope of the present invention. The liquid curable silicone elastomer composition may thus be free of pot life extender.

[0064] Examples of flame retardants include aluminium trihydrate, magnesium hydroxide, calcium carbonate, zinc borate, wollastonite, mica and chlorinated paraffins, hexabromocyclododecane, triphenyl phosphate, dimethyl methylphosphonate, tris(2,3-dibromopropyl) phosphate (brominated tris), and mixtures or derivatives thereof.

[0065] Examples of lubricants include tetrafluoroethylene, resin powder, graphite, fluorinated graphite, talc, boron nitride, fluorine oil, silicone oil, phenyl functional silicone oil, molybdenum disulfide, and mixtures or derivatives thereof.

[0066] Further additives include silicone fluids, such as trimethylsilyl or OH terminated siloxanes. Such trimethylsiloxy or OH terminated polydimethylsiloxanes typically have a viscosity < 150 mPa.s. When present such silicone fluid may be present in the liquid curable silicone elastomer composition in an amount ranging of from 0.1 to 5% weight, based on the total weight of the composition. Other additives include silicone resin materials, which may or may not contain alkenyl or hydroxyl functional groups.

[0067] Examples of pigments include carbon black, iron oxides, titanium dioxide, chromium oxide, bismuth vanadium oxide and mixtures or derivatives thereof.

[0068] Examples of colouring agents include vat dyes, reactive dyes, acid dyes, chrome dyes, disperse dyes, cationic dyes and mixtures thereof.

[0069] Examples of adhesion promoters include silane coupling agents, alkoxysilane containing methacrylic groups or acrylic groups such as methacryloxymethyl-trimethoxysilane, 3-methacryloxypropyl-tirmethoxysilane, 3-methacryloxypropyl-methyldimethoxysilane, 3-methacryloxypropyl-dimethylmethoxysilane, 3-methacryloxypropyl-triethoxysilane, 3-methacryloxypropyl-methyldiethoxysilane, 3-methacryloxyisobutyl-trimethoxysilane, or a similar methacryloxy-substituted alkoxysilane; 3-acryloxypropyl-trimethoxysilane, 3-acryloxypropyl-methyldimethoxysilane, 3-acryloxypropyl-dimethyl-methoxysilane, 3-acryloxypropyl-triethoxysilane, or a similar acryloxy-substituted alkyl-containing alkoxysilane; zirconium chelate compound such as zirconium (IV) tetraacetyl acetonate, zirconium (IV) hexafluoracetyl acetonate, zirconium (IV) trifluoroacetyl acetonate, tetrakis (ethyltrifluoroacetyl acetonate) zirconium, tetrakis (2,2,6,6-tetramethyl-heptanethionate) zirconium, zirconium (IV) dibutoxy bis(ethylacetonate), diisopropoxy bis (2,2,6,6-tetramethyl-heptanethionate) zirconium, or similar zirconium complexes having β-diketones (including alkyl-substituted and fluoro-substituted forms thereof); epoxy-containing alkoxysilanes such as 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl triethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 4-glycidoxybutyl trimethoxysilane, 5,6-epoxyhexyl triethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, or 2-(3,4-epoxycyclohexyl) ethyltriethoxysilane.

[0070] Examples of chain extenders include disiloxane or a low molecular weight polyorganosiloxane containing two silicon-bonded hydrogen atoms at the terminal positions. The chain extender typically reacts with the alkenyl groups and/or alkynyl groups of polydiorganosiloxane polymer (i), thereby linking two or more molecules of polydiorganosiloxane polymer (i) together and increasing its effective molecular weight and the distance between potential cross-linking sites.

[0071] A disiloxane is typically represented by the general formula $(HR^a{}_2Si)_2O$. When the chain extender is a polyorganosiloxane, it has terminal units of the general formula $HR^a{}_2SiO_{1/2}$ and non-terminal units of the formula $R^b{}_2SiO$. In these formulae, R^a and R^b individually represent unsubstituted or substituted monovalent hydrocarbon groups that are free of ethylenic unsaturation, which include, but are not limited to alkyl groups containing from 1 to 10 carbon atoms, substituted alkyl groups containing from 1 to 10 carbon atoms such as chloromethyl and 3,3,3-trifluoropropyl, cycloalkyl groups containing from 3 to 10 carbon atoms, aryl containing 6 to 10 carbon atoms, alkaryl groups containing 7 to 10 carbon atoms, such as tolyl and xylyl, and aralkyl groups containing 7 to 10 carbon atoms, such as benzyl.

[0072] Further examples of chain extenders include tetramethyldihydrogendisiloxane or dimethylhydrogen-terminated polydimethylsiloxane.

[0073] Where the optional additives may be used for more than one reason e.g. as a non-reinforcing filler and flame retardant, when present they may function in both roles. When or if present, the aforementioned additional ingredients are cumulatively present in an amount of from 0.1 to 30%wt, alternatively of from 0.1 to 20%wt based on the weight of the composition.

[0074] In order to prevent premature cure in storage, the composition will be stored prior to use in two parts Part A and part B. Typically part A will contain some of polydiorganosiloxane polymer (i) and reinforcing filler (ii) and hydrosilylation catalyst (iv) and part B will contain the remainder of polydiorganosiloxane polymer (i) and reinforcing filler (ii) together with components organohydrogenpolysiloxane (iii) and, if present, the inhibitor. The two part composition may be designed to be mixed together in any suitable ratio, dependent on the amounts of polydiorganosiloxane polymer (i) and reinforcing filler (ii) in part B and as such can be mixed in a Part A : Part B weight ratio of from 15 : 1 to 1 : 1.

[0075] The individual parts of the composition may be prepared in any way suitable. Any mixing techniques and devices described in the prior art can be used for this purpose. The particular device to be used will be determined dependent on the viscosities of ingredients and the final curable coating composition. Suitable mixers include but are not limited to paddle type mixers and kneader type mixers. Cooling of ingredients during mixing may be desirable to avoid premature curing of the composition.

[0076] The order for mixing ingredients when preparing the part A and part B compositions is not critical herein. Suitable parts A and B are prepared and then part A and part B are mixed together shortly prior to use.

[0077] When Part A and Part B are mixed together, the silicone rubber composition disclosed herein may comprise:

Polydiogansiloxane (i) in an amount of 30 to 75% by weight of the composition, reinforcing filler (ii) in an amount of from 5 to 40%wt, alternatively of from 5 to 30%wt, alternatively from 7.5 to 30%wt alternatively from 10 to 30% wt of the composition; organohydrogenpolysiloxane (iii) in an amount of from 0.5 to 10 weight %, alternatively from 1 to 10% by weight, alternatively from 2% to 10% by weight of the composition, hydrosilylation catalyst (iv) in an amount of from 0.01 to 1% of the composition;

optional resin (v) may be present in an amount of from 0 to 40% of the total composition

and when present inhibitor may be present in an amount of from an amount of from 0.0125 to 10% by weight of the composition. It will be appreciated that for all compositions the total weight % is 100 weight %.

[0078] The silicone rubber composition may, dependent on viscosity and application etc., be further processed by injection moulding, encapsulation moulding, press moulding, dispenser

moulding, extrusion moulding, transfer moulding, press vulcanization, centrifugal casting, calendering, bead application or blow moulding.

[0079] Curing of the silicone rubber composition may be carried out as required by the type of cure package utilized. Whilst it is usually preferred to use raised temperatures for curing hydrosilylation cure systems e.g. from about 80°C to 150°C, subsea silicone rubber compositions are generally designed to be cured at lower temperatures, e.g. between room temperature and 80°C, alternatively between room temperature, i.e. about 23-25°C to about 50°C. The composition herein will produce an elastomeric thermal insulation material which is resistant to cracking and or splitting under thermal and/or mechanical stress.

[0080] The composition as disclosed herein and resulting elastomer provided upon cure of the composition may be utilised for any suitable application requiring an elastomeric subsea insulation silicone rubber material made by curing the composition as hereinbefore described.

[0081] Elastomeric subsea insulation silicone rubber material as hereinbefore described may be utilised in the thermal insulation of, for example, piping including riser pipes, wellheads, Xmas trees, spool pieces, manifolds, risers and pipe field joints. Clearly any insulation material or system must be capable of being easily formed into complex shapes to accommodate the components of a pipe line assembly. In this case the relatively low viscosity of the pre-cured composition allows the composition to be pumped into prepositioned molds in order to enable the composition to cure into the shapes required to insulate the part concerned.

[0082] The following examples, illustrating the compositions and components of the compositions, elastomers, and methods, are intended to illustrate and not to limit the invention.

EXAMPLES

[0083] In the following examples, the unsaturated group (alkenyl and/or alkynyl), typically vinyl and Si-H content of polymers was determined using quantitative infra-red analysis in accordance with ASTM E168. All viscosities were measured in accordance with ASTM 1084 using a Brookfield rotational viscometer with the most appropriate spindle for the viscosity being measured at 1 rpm, unless otherwise indicated.

[0084] Two part compositions were prepared for the examples. The Part A composition is described in Table 1 below and was used as standard for all examples. A base was first prepared by mixing the polymer, resin and filler ingredients and the remaining ingredients were added subsequent to the preparation of the base.

Table 1. Part A composition used in all the following compositions.

Component	**Wt.%**
Dimethyl vinyl terminated polydimethylsiloxane (viscosity 53,000 mPa.s at 25°C and 0.23 wt.% vinyl) (i)	1.97
vinyl terminal polydimethylsiloxane (viscosity 53,000 mPa.s at 25°C and 0.08 wt.% vinyl (i)	32.44
A 65 : 35 weight % ratio of dimethylvinyl terminated polydimethylsiloxane polymer having a viscosity of 2000mPa.s and a vinyldimethylsiloxy capped MQ resin having 0.70 wt.% vinyl and a viscosity of 25 mPa.s (v)	41.17
Fumed silica filler (E) having a surface area of approximately 420m^2/g which had been hydrophobically treated with tetramethyldivinyldisilazane resulting in a vinyl content of 0.079 mmol/g (ii)	15.12
Karstedt's catalyst (divinyltetramethyldisiloxane complex of platinum) containing platinum (iv)	0.69
trimethylsiloxy terminated polydimethylsiloxane having a viscosity of 5000mPa.s	5.09

[0085] To exemplify (a) where the molar ratio of Si-H to vinyl is < 1.5 : 1 and the molar ratio of D^1 :D^2 is > 1 : 1, Part B compositions were prepared using several alternative trimethyl terminated dimethyl methyl hydrogen siloxanes as depicted in Table 2 in which the reference cross-linker had the structure $MD^1_{3.34}D^2_{5.32}M$, cross-linker 1 had the structure $MD^1_{8.7}D^2_{3.7}M$ and cross-linker 2 $MD^1_{5.9}D^2_{3.9}M$.

Table 2. Key components of the curing agent components in the rubber sample.

Component	Ref. (wt%)	Ex. 1 (wt%)	Ex. 2 (wt. %)
Dimethyl vinyl terminated polydimethylsiloxane (viscosity 53,000 mPa.s at 25°C and 0.23 wt.% vinyl). (i)	57.67	46.07	57.4
2,4,6,8-tetramethyl-2,4,6,8-tetramethylcyclotetrasiloxane (inhibitor)	1.0	0.5	0.5
tris[(1,1-dimethyl-2-propynyl)oxy]methylsilane	0.13	0.06	0.6
Ref Cross-linker (iii)	41.20	-	
Cross-linker 1 (iii)		52.8	
Crosslinker 2 (iii)			42
Molar ratio Si-H to unsaturated groups (vinyl) in 10:1 samples.	2:1	1.26:1	1.26
molar ratio of D^1 : D^2	0.6	2.4	1.5

[0086] Curing agent was prepared as follows by mixing all the ingredients together.

Preparation of rubber samples

[0087] All rubber samples were freshly-prepared prior to each study. Each sample involved a 10:1 weight ratio of Part A to Part B. The respective amounts of Parts A and B were introduced into a plastic cup (polypropylene, type = Max 40) and was then mixed by stirring in a dual-axis speed-mixer (model = DAC 150.1 FVZ-K, Hauschild) at 3000 rpm for about 30 seconds at room temperature to yield a single-phase bubble-free curable composition.

Thermal stability testing

[0088] A two-step protocol was used to assess the thermal stability of the cured materials at 180 °C in a nitrogen environment.

1. Samples were cured at 40 °C for a period of two hours between two parallel-plate sample fixtures (disposable, aluminum, 25-mm-diameter, 1-mm gap between plates) strain-controlled rotational rheometer (ARES-G2 from TA Instruments). This first low-temperature step is designed to mimic the curing of the silicone rubber material under end-use conditions. This temperature would be relevant to curing the rubber in a tropical climate.
2. The cured silicone rubber materials were then heated rapidly at a rate of 28 °C/min for approximately 5 minutes to reach a temperature of 180 °C in the rheometer. The modulus G^* was then determined at 180 °C for 20 to 24 h. In the process the modulus is determined approximately every 20 seconds and as such can result in over 5500 data points.

[0089] There are at least three features appearing in the time-resolved G* data measured at temperature T for all rubbers. At short times (< 5 minutes), the modulus grows very rapidly as the temperature approaches and reaches the target temperature. Modulus growth here is assumed to complete the curing reactions forming the 3D network structure. The modulus falls (or grows) at intermediate times (5 minutes to 10 hours) but at a much slower rate than that at short times. Ultimately, the modulus falls (or grows) at an even slower rate when held at 180 °C for more than ten hours. The modulus data are fit to a linear regression ($|G^*| = |G^*|_0 + t \bullet d|G^*|/dt$) for times of ten or more hours. The slope of this data, $d|G^*|/dt$, is called the modulus loss rate, and is used henceforth as a key metric of the thermal stability at 180 °C.

Results of Rubber Thermal stability testing

[0090] The rubber is stable only when $d|G^*|/dt$ is zero. Negative values indicates losses of the rubber mechanical properties with storage time at temperature T. Positive values indicate gains in the rubber mechanical properties with storage time at temperature T. Typical values of the modulus

loss rate d|*G**|/d*t* at 180 °C for rubbers prepared with and without additives are summarized in Tables 3a and 3b. Any additive option elevating d|*G**|/d*t* relative to that (-1111 Pa/h) without an additive indicates enhanced rubber thermal stability.

A significantly improved d|*G**|/d*t* has been observed for rubbers based on Example 2 and a positive value was achieved in the case of Example 1.

Table 3

Sample	**d|*G**|/d*t* (Pa/h)**
Reference	-916
Example 1	283
Example 2	**-464**

Tensile testing

[0091] Plaques for this test were made using freshly prepared rubber samples. The chases used to make the LSR plaques had nominal dimensions of 120mm x 120mm x 2mm thick. Each sample involved a 10:1 weight ratio of Part A to Part B, respectively. About 60 grams of Part A was weighed into a plastic cup (polypropylene, type = Max 200). This was then placed into a vacuum oven at room temperature and full vacuum was applied for 10 minutes. The cup was then removed from the oven and the appropriate amount of Part B was added to the Part A composition. The sample was then mixed using a dual-axis speed mixer (model = DAC 600 FVZ sp, Hauschild) at 2400 rpm for 30 seconds at room temperature to yield a single-phase bubble-free colorless viscous fluid. This viscous fluid was then poured into a molding chase. A Teflon-coated sheet of aluminum was positioned between the chase and the metal support plate to create a defect free surface to cast on. The freshly poured material and substrate was then placed back into a vacuum oven at room temperature and full vacuum was applied for about 10 min (depending on the viscosity of the corresponding mixture). The plaque was then removed from the oven and any bubbles that were created during the vacuum step were popped using a syringe. Finally, the plaque was placed on a level surface in a fume hood and allowed to sit undisturbed at room temperature until curing was complete.

[0092] Once the plaque was fully cured it was removed from the chase and any excess material was trimmed from its edges. Plaques were fabricated and microtensile specimens were punched out using NAEF punch press for tensile testing. Tensile test was conducted on an electromechanical test frame, INSTRON 5566, at a test speed of 6.67"/min (16.94cm/min).. As tensile strength is found to be a function of thickness for specimen thickness <2 mm, and constant for specimen thickness >2 mm, all the experiments were conducted on specimens with thickness > 2 mm.

Wet-aging testing

[0093] Studies of the rubber thermal and hydrolytic stability at elevated pressure are called wet-aging tests for simplicity. These studies involved the insertion of the rubber tensile bars into metal tubes (Swagelok); screw-on caps on the tube ends enabled the tubes to contain the water and pressure. The metal tubes with end caps were rated for pressure up to 3100 psi (21.37MPa) and temperature > 300 °C which is much higher than the operating pressure and temperature of the planned lab scale testing. Microtensile bars were placed in the metal tubes with 90% of the volume filled with water. Wet aging were conducted at 150°C for all new samples and 180°C for some selected samples. For the wet-aging experiments, specimens were taken out of the metal tubes after 7, 28, 49, and 91 days. The aging process was discontinued for samples once no improved thermal stability than the control was shown.

Results of rubber tensile strength testing

Table 4. Room-temperature tensile strength (MPa) of rubbers with new Si-H crosslinkers as a function of wet aging time at 150°C.

	Ratio of Si-H/Si-vi	0 days	7 days	28 days	49 days	91 days
Reference	2 : 1	5.300	4.850	3.440	2.260	1.360
Example 1	1.26 : 1	4.220	4.610	3.720	2.080	1.545
Example 2	1.26:1	4.00	3.67	2.51	Not tested	Not tested

Results of rubber room-temperature elongation testing

Table 5. Room-temperature elongation (%) at break of rubbers with new Si-H crosslinkers as a function of wet aging time at 150°C.

	0 days	7 days	28 days	49 days	91 days
Control	365.990	162.830	122.100	82.420	73.480
Example 1	353.8	176.8	153.800	108.390	104.415
Example 2	263.0	165.6	125.4	Not tested	Not tested

[0094] The above was repeated for compositions in accordance with (b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1. Compositions were prepared using a further alternative trimethyl terminated dimethyl methyl hydrogen siloxane (cross-linker 3) in Table63 in which the reference cross-linker was the same as above and Cross-linker 3 had the structure had the structure $MD^1_{28}D^2_{42}M$.

Table 6. Key components of the Part B composition components in the rubber sample using cross-linkers in accordance with (b).

Component	control (wt%)	Example 3 (wt%)	Example 4 (wt%)
Dimethyl vinyl terminated polydimethylsiloxane (viscosity 53,000 mPa.s at 25°C and 0.23 wt.% vinyl) (i)	57.67	80.57	82.9
2,4,6,8-tetramethyl-2,4,6,8-tetramethylcyclotetrasiloxane (inhibitor)	1.0	1.0	1.0
tris[(1,1-dimethyl-2-propynyl)oxy]methylsilane	0.13	0.13	0.13
Ref Cross-linker (iii)	41.20	-	-
Crosslinker 3 (iii)		18.3	16.0
Cross-linker - Degree of polymerisation (DP)	10.7	60	60
Cross-linker molar ratio of D^1 :D^2	0.6	0.6	0.6

The same test methods were used as described above.

Results of Rubber Thermal stability testing

[0095] Typical values of the modulus loss rate $d|G^*|/dt$ range from a very negative value (-916±7 Pa/h) of the Reference material to values as high as 283±59 Pa/h (Example 1). All negative values indicate an unstable rubber at 180 °C. The negative value for the control rubber is consistent with the expectation that it is unstable for temperatures at or above 180 °C. In contrast, a $d|G^*|/dt$ value of zero should be stable (by definition), and a value exceeding zero indicates modulus growth at 180 C. It is not expected that modulus growth will occur indefinitely even though the measured $d|G^*|/dt$ value in the experimental time window exceeds zero, since growth will eventually cease when all of one type of reactive groups (Si-H or vinyls) are consumed. A positive $d|G^*|/dt$ has been observed for rubbers based on three of the new curing agents (Example 1, 2). These curing agents are identified as promising candidates for further study.

Table 7. Modulus loss rate of the rubber thermal stability at 180 °C for rubbers based on curing agents.

Sample	**d|*G***|/d*t* (Pa/h)**
Reference	-916
Example 3	164
Example 4	-302

Results of rubber tensile strength testing

Table 8. Room-temperature tensile strength (MPa) of rubbers with new Si-H crosslinkers as a function of wet aging time at 150°C.

	Ratio of Si-H/Si-vi	0 days	7 days	28 days	49 days	91 days
Reference	2 : 1	5.300	4.850	3.440	2.260	1.360
Example 3	1.26 : 1	4.04	4.400	3.370	2.610	1.140
Example 4	1.10 : 1	4.15	4.4	3.380	2.650	1.160

Table 9. Room-temperature elongation at break (%) of rubbers with new Si-H crosslinkers as a function of wet aging time at 150°C.

	0 days	7 days	28 days	49 days	91 days
Reference	365.990	162.830	122.100	82.420	73.480
Example 3	377.64	191.020	173.060	143.170	74.250
Example 4	441.85	218.18	167.240	165.340	119.790

CLAIMS

WHAT IS CLAIMED IS:

1. A subsea insulation silicone rubber composition comprising

(i) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is $–[OSiR_2]$ - and D^2 is –[OSiRH]-;

(iv) a hydrosilylation catalyst and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{(3-d)} SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2;

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 :D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1.

2. A subsea insulation silicone rubber composition in accordance with claim 1 wherein in (a) the molar ratio of Si-H to unsaturated groups is < 1.35 : 1.

3. A subsea insulation silicone rubber composition in accordance with any preceding claim wherein claim 1 wherein in (a) the molar ratio of D^1 : D^2 is > 1.25 : 1.

4. A subsea insulation silicone rubber composition in accordance with claim 1 wherein in (b) the degree of polymerisation of cross-linker (iii) is > 40.

5. A subsea insulation silicone rubber composition in accordance with claim 1 wherein in (b) the molar ratio of $D^1 : D^2$ is from 0.5 : 1 to 0.8 : 1.

6. A subsea insulation silicone rubber composition in accordance with any preceding claim which composition also includes one or more additives selected from, inhibitors, non-reinforcing fillers, electrical conductive fillers, thermally conductive fillers, non-conductive filler, pot life extenders, flame retardants, pigments, colouring agents, adhesion promoters, chain extenders heat stabilizers, compression set improvement additives and mixtures thereof.

7. A subsea insulation silicone rubber composition in accordance with any preceding claim which composition is stored prior to use in two parts.

8. An elastomeric subsea insulation silicone rubber material which is the cured product of a composition in accordance with any one of claims 1 to 7.

9. An elastomeric subsea insulation silicone rubber material which is obtainable or obtained by curing a composition comprising

(j) one or more polydiorganosiloxane polymer(s) having a viscosity of from 1000 to 500,000mPa.s at 25°C containing at least two alkenyl groups and/or alkynyl groups per molecule;

(ii) one or more reinforcing fillers; and

a hydrosilylation catalyst package comprising

(iii) an organohydrogenpolysiloxane polymer having at least 2, alternatively at least 3 Si-H groups per molecule of the structure

$R^2_z (H)_{3-z}$ - Si-$D^1_n D^2_m$Si $(H)_{3-z} R^2_z$

Wherein R^2 is an alkyl group having from 1 to 10 carbons, z is 2 or 3, n and m are integers, D^1 is $–[OSiR_2]–$ and D^2 is –[OSiRH]-;

(iv) a hydrosilylation catalyst; and optionally

(v) an organosilicate resin comprising $R^4_d R^2_{3-d} SiO_{1/2}$ (M) siloxane units and $SiO_{4/2}$ (Q) siloxane units having a weight average molecular weight of from 3000 to 30,000 g/mol and a molar ratio of M groups : Q groups of from 0.60: 1 to 1.50 and wherein R^2 is as described above and R^4 is an alkenyl or alkynyl group having from 2 to 10 carbons and d is 0, 1 or 2

characterised in that either:

(a) the molar ratio of Si-H to unsaturated groups is < 1.5 : 1 and the molar ratio of D^1 :D^2 is > 1 : 1; or

(b) the degree of polymerisation of cross-linker (iii) is > 20 and the molar ratio of D^1 : D^2 is from 0.5 : 1 to 1 : 1.

10. A method of preparing an elastomeric subsea insulation silicone rubber material which is the cured product of a composition in accordance with any one of claims 1 to 7 by mixing and curing said composition.

11. Use of a silicone rubber composition in accordance with any one of claims 1 to 7

to make an elastomeric subsea insulation silicone rubber material.

12. Use in accordance with claim 11 to make a subsea article containing said elastomeric subsea insulation silicone rubber material.

13. Use in accordance with claim 12 wherein said subsea article is selected from piping wellheads, Xmas trees, spool pieces, manifolds, risers and pipe field joints.

14. A subsea article insulated at least partially by an elastomeric subsea insulation silicone rubber material in accordance with claim 8 or 9.

15. A subsea article in accordance with claim 14 wherein the subsea article is selected from piping wellheads, Xmas trees, spool pieces, manifolds, risers and pipe field joints.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/067115

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L83/04 E21B17/01 E21B36/00 F16L59/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E21B C08G F16L C08L C09D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 2014/046310 A1 (DOW CORNING TORAY CO LTD [JP]) 27 March 2014 (2014-03-27) table 4	1-15
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A	WO 2013/178992 A1 (ADVANCED INSULATION PLC [GB]) 5 December 2013 (2013-12-05) example 1 claims 1,9,14	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A,P	WO 2019/024432 A1 (DOW SILICONES CORP [US]; GAO JIANJUN [CN] ET AL.) 7 February 2019 (2019-02-07) example 3	1-15
A,P	WO 2018/229479 A1 (ADVANCED INSULATION LTD [GB]) 20 December 2018 (2018-12-20) page 7, line 1 - page 8, line 2	1-15

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